

The acid-base condition in vegetation, litter and humus: III. Acidoid formation in relation to base status.

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A high degree of correlation has been shown to exist between the acids and acidoids and the bases in the living plant and in the mature litter of several species (cf. part I of this series). A certain relationship was also found to exist between the base status of the soil and the base, and acid and acidoid content of beech leaves and spruce needles (cf. part II).

In the aerobic decomposition of the mature litter the acidoid content (per 100 g. organic matter) increased considerably, the increase being greater the greater the base content of the materials, except in the case of materials whose original acidoid content is very high as in the leaves of elm and ash (cf. table 18 $\frac{1}{2}$).

In some cases, in which the decomposition was not too great (wheat straw, pine needles, beech leaves) the production of acidoids compensated the relative increase in bases resulting from the decomposition. In the case of wheat straw an absolute gain in acidoids could be recorded at the end of one year. In the case of litter, the acidoid content of which is greater than that of many forms of humus and which decompose very rapidly (elm and ash leaves) there was a considerable absolute loss of acidoids in spite of the fact that the acidoid content per 100 gram had increased.

Within certain limits, nature apparently compensates the increase in basicity resulting from decomposition of the organic matter by increasing the base binding capacity of the organic residue. The increase in pH which rapidly takes place as a result of an early destruction of the soluble organic acids may be assumed to be responsible for the increased oxidation which leads to the production of acidoids. This compensatory process is, of course, of the greatest importance from the point of view of soil formation and soil fertility because the acidoids not only keep the reaction within

Table 18 ¹/₂. *The relationship between the »excess base» content and the acidoid formation in decomposing litter. Aerobic series without leaching. Materials arranged in the order of base content per pot of 100 grams air dry litter.*

| Material | Excess base per pot M.e. | Acidoids: | | | | | |
|--------------------|--------------------------------|-------------------------------|-----------------|-------------------------------|-----------------|---------------------------------------|-----------------------------------|
| | | Originally present: | | At end of 1 year: | | Gain M.e./100 g. org. matter | Gain or loss (-) per pot |
| | | M.e./100 g. org. matter | M.e. per pot | M.e./100 g. org. matter | M.e. per pot | | |
| | | a | b | c | d | c-a | d-b |
| Wheat straw | 35.6 | 16.1 | 13.0 | 37.9 | 16.3 | 21.8 | 3.3 |
| Pine needles | 39.4 | 38.0 | 33.7 | 66.1 | 31.7 | 28.1 | -2.0 |
| Beech leaves | 70.2 | 70.5 | 60.8 | 122.2 | 58.7 | 51.7 | -2.1 |
| Alder » | 80.3 | 101.9 | 84.8 | 149.2 | 63.1 | 47.3 | -21.7 |
| Oak » | 90.2 | 91.7 | 76.6 | 137.5 | 62.4 | 45.8 | -14.2 |
| Maple » | 123.2 | 101.9 | 81.9 | 171.8 | 59.3 | 69.9 | -22.6 |
| Birch » | 128.0 | 87.6 | 73.7 | 158.2 | 59.2 | 70.6 | -14.5 |
| Elm » | 231.6 | 181.5 | 118.3 | 202.1 | 46.1 | 20.6 | -72.2 |
| Ash » | 234.8 | 134.1 | 102.9 | 185.0 | 41.8 | 50.9 | -61.1 |

certain limits by neutralizing the bases but they also bring about a fixation of the latter and thus reduce losses by leaching.

The present work is a report on our investigation of the influence of the base status on the formation of acidoids in laboratory experiments as well as in nature.

The decomposition experiments here described were carried out in the same manner as the experiments described in Part I of this series. In order to determine the influence of lime on the formation of acidoids in various types of materials the V, F₁, F₂ and H samples of the Häggbygget podzol were decomposed with and without the addition of lime during a period of one year. The V sample consisted largely of a mixture of the leaves and twigs of *Vaccinium* and *Caluna vulgaris*. The acidoid content, the pH, and the pH_u in N.KCl solution before and after the treatment are shown in table 19.

The significant facts from the point of view of our present study may be summed up as follows:

1. Without lime there is a small to moderate (8.7—20.5 m.e.) increase in acidoids per 100 grams in the F and V samples whereas the H sample has suffered a small decrease during the transformation. There is no absolute gain in acidoids, the quantity per pot having decreased in every case without lime.

2. With lime there is a considerable increase (36.2—62.9 m.e.) in acidoids per 100 grams in all samples, and this increase is so great that, in spite of the loss in organic matter by decomposition, there is an absolute gain in acidoids.

3. With an increase in the acidoid content there is a decrease

Table 19 a. *The influence of lime on the formation of acidoids in the V, F₁, F₂ and H samples of the Haggbygget podzol. Aerobic decomposition for one year without leaching. 10 g. CaCO₃ per pot of 100 g. air dry material.*

| Sample | Percentage decomposition: | | M.e. Acidoids: | | | | | |
|----------------------|---------------------------|-----------|-------------------------|--------------|-----------|----------|--------------|-----------|
| | | | per 100 g. org. matter: | | | per pot: | | |
| | without lime | with lime | Original | Transformed: | | Original | Transformed: | |
| | | | | without lime | with lime | | without lime | with lime |
| V | 29.0 | 33.0 | 50.3 | 69.6 | 113.2 | 43.4 | 42.7 | 65.4 |
| F ₁ | 29.8 | 34.0 | 63.8 | 84.3 | 112.9 | 54.9 | 50.9 | 64.1 |
| F ₂ | 9.9 | 16.8 | 85.0 | 93.7 | 128.7 | 67.9 | 67.4 | 85.5 |
| H | 8.5 | 16.9 | 105.0 | 100.9 | 141.2 | 79.8 | 70.9 | 90.0 |

Table 19 b. *The pH and pH_u of the original and transformed samples in table 19 a.*

| Sample | pH in water: | | | pH _u in N.KCl: | | |
|----------------------|--------------|--------------|-----------|---------------------------|--------------|-----------|
| | Original | Transformed: | | Original | Transformed: | |
| | | without lime | with lime | | without lime | with lime |
| V | 4.44 | 6.24 | 7.11 | 2.50 | 2.26 | 2.00 |
| F ₁ | 4.28 | 4.37 | 7.17 | 2.37 | 2.25 | 2.05 |
| F ₂ | 4.14 | 4.25 | 7.24 | 2.28 | 2.24 | 1.99 |
| H | 3.71 | 3.96 | 7.35 | 2.24 | 2.37 | 1.95 |

in the pH_u values. These are therefore lowest in the lime treated samples, i.e., in those samples which, during the decomposition, had the highest pH.

Table 20 gives the results of a similar experiment carried out with wheat straw to which, in addition to lime, nutrient salts were also added.

We note the following:

1. Lime alone has here but little effect on the acidoid production and no effect on the decomposition. *Explanation:* The pH of the material was equally high without lime and lime itself is no nutrient.
2. With lime and nutrient salts there is a great increase both in the decomposition and in the synthesis of acidoids. The latter is so great that in spite of an extensive destruction of organic matter there is a considerable absolute gain in acidoids as compared to the sample receiving no addition.
3. With nutrient salts alone there is a considerable increase both in the decomposition and in the production of acidoids but

the latter is here only great enough to keep the quantities of acidoids per pot at approximately the same level as in the sample receiving no addition.

Conclusion: The synthesis of acidoids is, at ordinary soil reactions, a biochemical process which is favored by a high pH.

Table 20. *The influence of lime and nutrient salts on the formation of acidoids in wheat straw during one year aerobic decomposition.*

| Treatment per 100 g. | Decomposition % | pH | M.e. acidoids: | |
|----------------------------------------------------|-----------------|------|---------------------------|---------|
| | | | per 100 g. organic matter | per pot |
| Undecomposed straw | — | 6.14 | 16.1 | 13.0 |
| Decomposed: | | | | |
| No addition | 46.5 | 7.32 | 37.9 | 16.3 |
| 10 g. CaCO ₃ | 45.5 | 7.23 | 39.6 | 17.4 |
| 10 g. CaCO ₃ + salts ¹ | 77.2 | 7.80 | 122.0 | 22.4 |
| Salts alone ¹ | 66.3 | 6.35 | 62.0 | 16.9 |

In view of the results thus far obtained we should expect a marked difference in the acidoid content of the humus from neutral low-moors and acid highmoors. The acidoid content should be higher and the ultimate pH should be lower in the former than in the latter.

That this prediction is correct is shown in table 21 which gives the acid-base conditions in a vertical series of samples from one of each of these types of peat formations.

The Mölnér samples are from the village of Mölnér by Väte on the calcareous island of Gothland. Samples I and II consist of amorphous, almost black granules whereas sample III, which is less decomposed, is fibrous and brown in color. At 60 cm there was a sharp transition to the almost white, stratified layer of precipitated chalk. The moor is cultivated.

The Annerstad samples are from the «wet end» of the hydrologic series of podzol profiles which have been discussed in a previous publication (LÖNNEMARK, WIKLANDER & MATTSO 1940). Only 5 of the 11 samples collected are included in this work.

The most important facts in table 21 may be summed up as follows:

1. The Mölnér samples I and II possess the highest acidoid content we have thus far found in any natural sample of humus. Sample III lags far behind the two upper samples with respect to its acidoid (and base) content, a fact which we ascribe to anaerobic conditions

¹ 2 g. (NH₄)₂SO₄ + 2 g. K₂HPO₄.

Table 21. *The acid-base conditions (a) in the base saturated humus from the Mölner moor on the island of Gothland and (b) in the unsaturated humus from the Annerstad highmoor in Småland.*

(a) Mölner series:

| No | Depth cm | Loss on ignition % | pH | M.e./100 g. organic matter: | | | | $\frac{H+B}{B} = \frac{A+a}{B}$ | pH _u in: | | w—s |
|-----|-------------|-----------------------------|------|-----------------------------|------------|---------------|-----------------------|---------------------------------|---------------------|------------|------|
| | | | | Acidity H | Bases B | Acidoids A | Org. acids H+B—A=a | | water w | N.KCl s | |
| I | 0—10 | 81.46 | 6.31 | 11.3 | 282.3 | 266.8 | 26.8 | 1.04 | 2.07 | 1.74 | 1.23 |
| II | 15—25 | 83.20 | 6.34 | 11.9 | 282.5 | 267.5 | 26.9 | 1.04 | 2.99 | 1.73 | 1.26 |
| III | 40—50 | 89.82 | 6.30 | 9.0 | 175.9 | 148.5 | 36.4 | 1.05 | 3.18 | 1.97 | 1.21 |

(b) Annerstad series:

| | | | | | | | | | | | |
|----|---------|-------|------|-------|------|-------|------|-----|------|------|------|
| I | 5—10 | 95.11 | 3.37 | 108.2 | 25.5 | 126.0 | 7.7 | 5.2 | 2.74 | 2.03 | 0.71 |
| IV | 40—45 | 98.10 | 3.41 | 102.0 | 14.6 | 112.5 | 4.1 | 8.0 | 3.06 | 2.09 | 0.97 |
| VI | 60—65 | 98.91 | 3.26 | 111.2 | 14.2 | 117.0 | 8.4 | 8.8 | 2.86 | 2.07 | 0.79 |
| IX | 110—115 | 98.86 | 3.24 | 84.5 | 10.6 | 87.5 | 7.6 | 9.0 | 2.92 | 2.31 | 0.61 |
| X | 130—135 | 97.20 | 3.56 | 86.0 | 14.3 | 85.8 | 14.5 | 7.0 | 3.35 | 2.38 | 0.97 |

which, as we have seen (in Part I), are not conducive to the synthesis of acidoids.

2. The acidoid content in the Annerstad samples is less than half that of the upper Mölner samples. The acidoid content shows a general tendency to decrease downwards.

3. There are more organic acids in the base saturated Mölner than in the unsaturated Annerstad samples and in both series there is a maximum of acids in the deepest layer.

4. The ultimate pH in KCl solution is here again lower the higher the acidoid content and reaches a value as low as 1.73.

5. The exchange acidity (w—s) attains extraordinary high values in the Mölner samples.

Fig. 19 gives the titration curves of the two series before and after electrodialysis.

It is well known that the purely chemical oxidation of humus and other forms of organic matter is greatly accelerated in the air in the presence of alkalies (SHOREY 1930). One of the many questions which must be answered in connection with our present problem was how the treatment with alkali affects the acidoid content of humus.

To answer this question we treated 10 grams of each of the podzol samples described in table 19 with 200 cc 0.5 N.NaOH in wide porcelain dishes. The thin paste thus formed was frequently stirred and evaporated to dryness on the steambath on the third day. The samples were then electrodialysed, the anode solution was

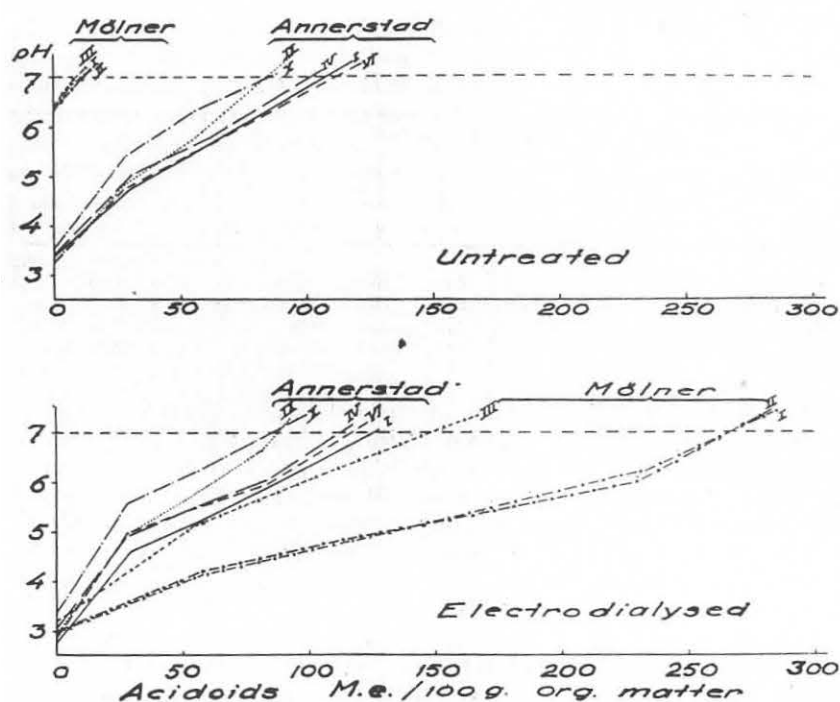


Fig. 19. Titration curves of the Annerstad highmoor and the Mölner lowmoor peat before and after electro dialysis (cf. table 21).

titrated for acids and the acidoids were afterwards titrated to pH 7 in the usual way. The results are shown in table 22.

We note that the alkaline treatment has brought about a great increase in both acids and acidoids — up to over 100 m.e. per 100 gram — and that the pH_u values have here, as in previous experiments, been lowered.

The great increase in acids indicates that, in addition to its oxidizing effect, the alkali has also caused a cleavage of the acidoids (actually ampholytoids) whereby diffusible units small enough to pass through the parchment paper are split off — analogous perhaps to the hydrolytic cleavage of the proteins and carbohydrates.

It should, however, be pointed out that the highly dispersed Na-humate is partly diffusible through the membrane employed and that the dark colored substances appearing in the anode solution are partly flocculated by Ca ions and to an even greater extent by Al and ferric ions (if the pH of the system be adjusted to the I.E.P.). The distinction between acids and acidoids on the basis of the definition here applied is, under such conditions, not sharp. It can

Table 22. *Acidoids and (electrodialysable) acids in the V, F₁, F₂ and H samples of the Haggbyget podzol and their pH_u before and after treatment with NaOH.*

| Sample | M.e./100 g. organic matter: | | | | | | pH _u in: | | | |
|----------------------|-----------------------------|------------|--------------|-------------|------------|--------------|---------------------|-------|--------|-------------------|
| | Acidoids: | | | Acids: | | | Water: | | N.KCl: | |
| | before b | after a | diff. a—b | before b | after a | diff. a—b | before | after | before | after |
| V | 50.3 | 119.8 | 69.5 | 33.8 | 113.0 | 79.2 | 3.27 | 2.78 | 2.50 | 1.98 |
| F ₁ | 63.8 | 153.7 | 89.9 | 20.2 | 119.3 | 99.1 | 3.16 | 2.79 | 2.37 | 1.93 |
| F ₂ | 85.0 | 188.3 | 103.3 | 14.2 | 123.8 | 109.6 | 3.22 | 2.77 | 2.28 | N.D. ¹ |
| H | 105.0 | 183.7 | 78.7 | 13.5 | 114.4 | 100.9 | 3.22 | 2.74 | 2.24 | N.D. ¹ |

safely be asserted that a part of the substances reported as acids in table 22 in reality are acidoids. But no sharp line can be drawn between acids and acidoids (molecular and colloidal dispersion). In humus we meet with a long range of dispersibility and we believe the dispersibility to be intimately related to the acidoid content, i.e., to the density of polar groups. The greater this polarity the greater the dispersing forces and the smaller the units capable of a separate existence.

Having found that a high base status favors the formation of acidoids by direct chemical action as well as biochemically in connection with microbial decomposition it remained to find out what a low base status would lead to in the case of material which is naturally rich in bases and acidoids and is therefore easily decomposed.

For this purpose decomposition experiments with completely electrodialysed elm and birch leaves were carried out in the same manner as described in part one. The experiment included two series one of which was unleached while the other was leached with 400 cc every two weeks, amounting to a total of 9 600 cc for the year. Each pot contained 100 grams of the air dry material and was inoculated with an extract of a mixture of garden soil and raw humus.

Before we discuss the final results (cf. table 23) of the decomposition a summary of our notes on the leaching will be in place.

In spite of the removal of practically all strong bases the elm leaves showed signs of great microbial activity while the birch leaves appeared quiescent. The composition of the leachings shown in fig. 20 and 21 gives us some insight into the process. Since the leachings reacted acidic — except for a short period in the case of the elm leaves — and contained no strong base cations, these figures have no curves for titrable base in the ashes as in fig. 1—4.

¹ Not determined due to insufficient material.

The originally light coloured leachings from the elm leaves changed in two to three months to an almost black solution which smelled strongly of ammonia.

The total amounts of organic matter (*g.*) and acids (*m.e.*) removed by leaching were in the elm leaves 12.33 and 11.24 and in the birch leaves 2.16 and 4.68 per 100 grams of dry matter respectively.

In addition to the free acids as determined by electrometric titration to pH 7, a certain amount was removed in combination with ammonia but this was not determined (cf. table 23).

Turning now our attention to the decomposition residue as presented in table 23 we note the following:

1. The decomposition is four times as great in elm as in birch leaves and is somewhat greater in the leached as compared to the unleached series. (The decomposition of the non-electrodialysed leaves was: elm 65.1 % and birch 55.5 %. Cf. table 16.)

2. The production of ammonia is much greater in elm than in birch leaves. In the unleached elm leaves the electrodialysable base mounts from zero to 84.1 m.e. per 100 grams organic matter. The production of ammonia expresses itself also in an increase in pH and a decrease in acidity (H).

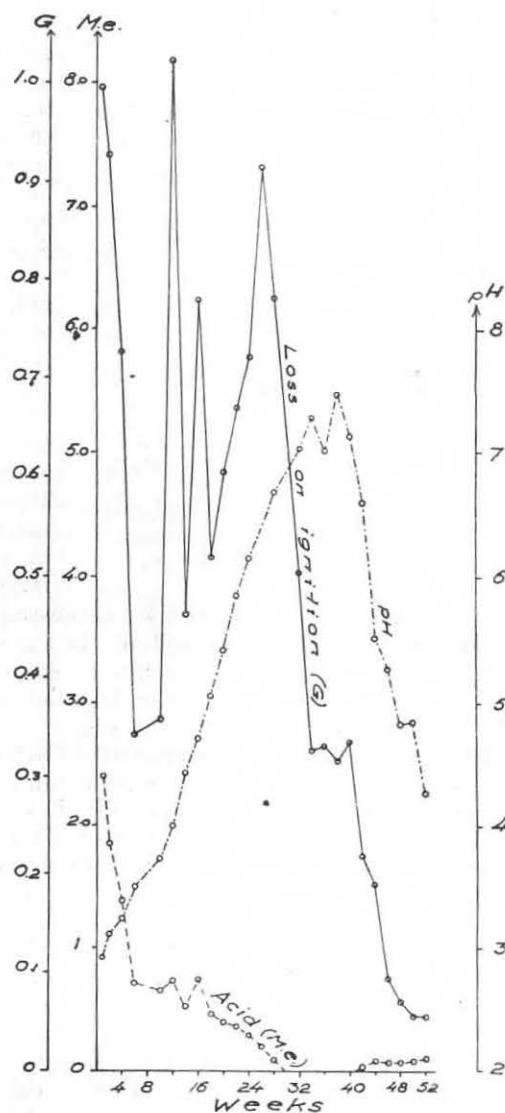


Fig. 20. Composition and pH of the 400 cc fortnightly leachings from decomposing, electro-dialysed elm leaves.

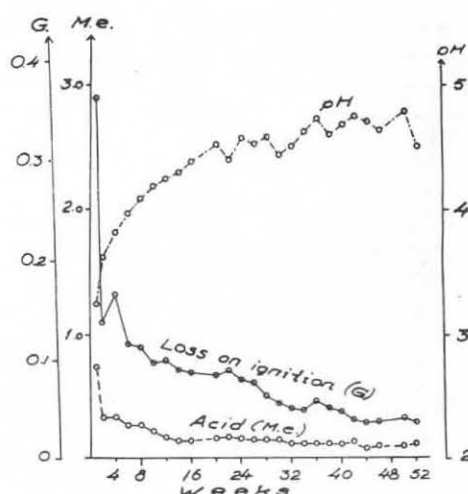


Fig. 21. Composition and pH of the 400 cc fortnightly leachings from decomposing, electrodialysed birch leaves.

3. The acidoid content per 100 grams organic matter has been decreased in every case but the decrease is greatest in that material in which this content was originally the highest, i.e., in the elm leaves. In the leached elm leaves the acidoid content has fallen to less than one third of the amount originally present. Even the sum of the final acidoids and acids is considerably smaller than the original acidoid content.

4. In harmony with the decrease in the acidoids there is an increase in the pH_u values. Due to an enrichment in the nitrogen content this increase in pH_u is out of proportion large in the case of elm leaves.

(The effect of nitrogen will be discussed in a later paper.)

The most significant result of the experiment is the decrease in the acidoid content. This seems to show that a high acidoid level cannot be maintained at a low base level even in such cases where the original acidoid content is high.

How then is this accomplished? It is improbable that the acidoid groups already present suffer a chemical reduction as a part of a reversible oxidation-reduction system whose equilibrium is a function of the pH. Under aerobic conditions there is probably no reduction of acidoids. The quantity of acidoids must be governed by an equilibrium between two steps in the oxidation of organic matter. In the first of these the acidoids are formed and in the second they are decomposed (to CO_2 and H_2O). The relative rate of these two oxidations must fix the acidoid level of the system, and any factor, e.g., the base status, which affects the two steps of oxidation differently will cause a change in the acidoid level. The mechanism by which the base status might be conceived to adjust the acidoid content in the way we have observed it can best be illustrated by referring to a familiar reaction cited at length by STIEGLITZ (1912):

Aldehydes are oxidized by an ammoniacal silver nitrate solution (the silver mirror test). The oxidation is much more rapid in the presence of alkali hydroxides. This is explained by STIEGLITZ as follows:

The aldehyde, e.g., formaldehyde, consists principally of a stable form CH_2O but contains a trace of an active form $CH(OH)$. This

Table 23 a. *The acid-base conditions before and after one year decomposition of electrodialysed elm and birch leaves with and without leaching.*

| Sample | Loss on ignition % | Decomposition % | pH | M.e./100 g. organic matter: | | | |
|----------------------------|-----------------------|--------------------|------|-----------------------------|-------------------------|---------------|-------------------------|
| | | | | Acidity H | Bases ¹ B | Acidoids A | Acids ² a |
| Elm: | | | | | | | |
| Before decomposition . . . | 87.28 | — | 2.90 | 181.5 | 0.0 | 181.5 | 0.0 |
| After 1 year (unleached) . | 70.78 | 60.1 | 5.84 | 39.6 | 84.1 | 110.8 | 30.5 |
| " " " (leached) . . . | 69.73 | 64.8 | 4.31 | 51.0 | 16.0 | 58.2 | 16.1 |
| Birch: | | | | | | | |
| Before decomposition . . . | 99.41 | — | 2.99 | 87.6 | 0.0 | 87.6 | 0.0 |
| After 1 year (unleached) . | 98.79 | 15.3 | 3.55 | 63.8 | 7.0 | 65.1 | 7.9 |
| " " " (leached) . . . | 98.70 | 16.1 | 3.52 | 62.3 | 7.0 | 68.4 | 5.7 |

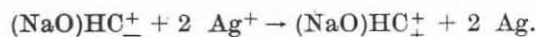
Table 23 b. *The pH_u in $N. KCl$ of the original and of the decomposed and, for the second time, electrodialysed material in table 23 a.*

| Sample | Original | Decomposed: | |
|-----------------|----------|-------------|----------|
| | | Unleached: | Leached: |
| Elm | 2.03 | 2.57 | 3.00 |
| Birch | 2.26 | 2.39 | 2.38 |

second form contains a hydroxyl group, an unsaturated divalent C atom, has acidic properties and is very sensitive to oxidation. The addition of alkali leads to the formation of the salt $CH(ONa)$. This disturbs the equilibrium between the two forms of aldehydes leading to an increase of the unsaturated and strongly reducing form thus



The oxidation which then proceeds rapidly is formulated as follows:



The disappearance of $2 Ag^+$ leaves $2 OH^-$ free to combine with the oxidized carbon:



thus forming Na-formate.

¹ By backward titration of the cathode solution to methyl orange. Bases mostly NH_3 with some M_2O_3 .

² By titration of anode solution to phenol phthalein.

STIEGLITZ then proves that the alkali acts on the aldehyde and not on the silver salt by measuring the potential difference between two platinum electrodes, one dipping into a solution of silver nitrate and the other into a solution of formaldehyde containing sodium nitrate, the two solutions being connected by a salt bridge. The extremely small potential between the silver nitrate and formaldehyde solutions was found to be enormously increased when sodium hydroxide was added to the aldehyde.

Substituting the formaldehyde in STIEGLITZ's experiment by humus we obtained the same effect: the addition of sodium hydroxide to the humus greatly increased the potential difference. The phenomena will be studied systematically and reported later.

Assuming a similar activation of the «colloidal aldehydes» by alkalies and by writing acidoid in place of formic acid in the last equation we obtain a satisfactory explanation of the relation between the base status and the acidoid content: At a high base status the oxidation of aldehydes — or other similarly reacting compounds — to acidoids takes place at a higher rate than the oxidation of acidoids to carbonic acid and water until a certain height in the acidoid level has been attained at which the two steps of oxidation may be assumed to proceed at the same speed. At a low base status there is an equilibrium between the two steps of oxidation at a lower acidoid level, and if the material is originally high in acidoids (as the electrodialysed elm leaves) these will be decomposed faster than they are formed in the decomposition residue.

We often hear the statement that fungi produce sour humus and that bacteria produce mild humus. But all humus is sour — when unsaturated with bases — and we have found the «mild» or neutral humus to be the most sour, i.e., the strongest acidoid, and the sour humus to be the least sour, i.e., the mildest acidoid. It is therefore not true that the fungi produce any particularly sour humus nor that they are responsible for the humus becoming sour. The sourness of humus is entirely a question of base status and is determined by (1) the original composition of the litter, (2) the rate of decomposition, (3) the acidoid formation and (4) the leaching. The undecomposed litter would in many cases be as sour as «sour» humus if completely unsaturated by leaching.

It is interesting to note that the same relationship between the base status and acidoid formation appears to exist in all of the three classes of substances investigated: the living vegetation V, the mature litter F and the humus H (cf. fig. 22). The acid vegetation and litter such as pine, spruce, etc. has, like the sour humus, a low acidoid content whereas the vegetation and litter high in bases such as elm, ash etc. has, like the mild humus a high acidoid content. By analogy we might conclude that the fungi belong to the former group whereas the bacteria belong to the latter group of organisms.

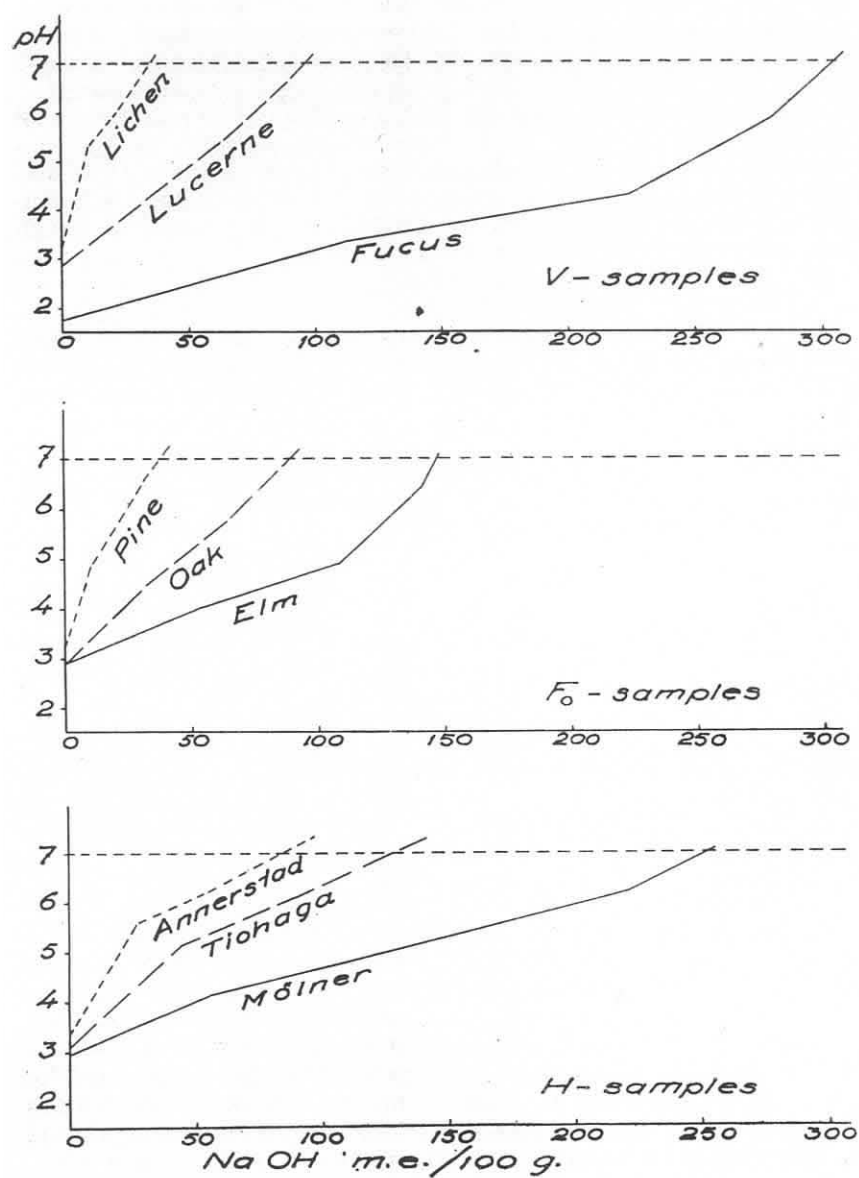


Fig. 22. Titration curves showing extremes in the capacity to bind base (= acid content) of electrolysed samples of vegetation (V), fresh litter (F₀) and humus (H).

Since the humus to a large extent consists of living microorganisms, of «microbial litter» and of the decomposition residue of these we can, if the analogy holds, see why the same principles which apply to the higher plants and their litter also applies to the humus.

The fungi live in sour humus probably because they have a small demand on bases. They do not make the humus sour. On the contrary they compensate, in accordance with the principle of Le Chatelier, the low base status by suppressing the strength and the quantity of acidoids. The bacteria, on the other hand, compensate a high base status by increasing the strength and quantity of the acidoids.

We cannot inquire into the nature of this intricate mechanism of compensation between acid and base in the oxidation of organic matter without being reminded of the striking analogy which exists between an acid and a reducing substance. According to Brönsted's generalized definition the relation between acid A and base B is:



i. e., the acid loses a proton and becomes a base.¹ When a reducing substance is oxidized it loses electrons:



It is of course not claimed that the two reactions are complementary since oxidation involves a change of valence whereas neutralization does not. But when the oxidation leads to the formation of an acid (or acidoid) it is reasonable to expect the neutralization of the acid to speed up the oxidation.

The protons may, at the moment of their release, collide with the reductant before they collide with a hydroxyl ion. The «nascent», unhydrated H ion may, in other words, accept an electron from the reductant and thus become the oxidizing agent. This might be illustrated by combining equations (1) and (2) and putting A in place of Ox thus



In the presence of oxygen or some other oxidant the nascent hydrogen would be reoxidized to H ions which would then in the normal way be neutralized. Even under anaerobic conditions the addition of alkali might stimulate the production of acids and acidoids. Hydrogen gas would then be evolved and the surplus of OH ions would supply the oxygen for the carboxyl groups. The effect of alkali on the formation of acidoids under anaerobic conditions has not yet been studied. Reversible oxidation-reduction equilibria would probably soon put a stop to the reaction.

In order to bring out the relationship between the base status and the acidoid content more clearly and to show its general applica-

¹ The anion of a weak acid is here defined as a base; it binds H ions.

tion to vegetation, litter and humus alike we have plotted the titration curves of three completely electro dialysed samples from each of the three groups of materials. Each group is represented by the extremes in acidoid content. A third sample was so chosen as to occupy an intermediate position (fig. 22).

The figure includes the following:

V samples:

1. Iceland moss (cf. table 1).
2. Lucerne (» » »)
3. Seaweed (*Fucus vesiculosus* from Kattegat).

F₀ samples:

1. Pine needles (cf. table 1).
2. Oak leaves (» » »)
3. Elm » (» » »)

H samples:

1. Annerstad (unsaturated anaerobic) (cf. table 21).
2. Tiohaga (» aerobic) (» » 16).
3. Mölner (saturated ») (» » 21).

The most striking thing in fig. 22 is the enormous capacity of the seaweed to bind base. Three species investigated showed capacities of 297, 303 and 305 m.e. per 100 grams. As here estimated the alga has an acidoid content which is about nine times that of the Iceland moss. But then the seaweed has developed under conditions of an extremely high base status, for in addition to the nearly neutral reaction of the seawater it contains large amounts of salts which greatly increase the effective base status (the capacity to bind base is greatly increased in the presence of salts).

In contrast to the algae the lichens develop mostly under conditions of very low base status on leached podzol and come seldom in contact with a solution much stronger than rain water.

If we are not going to dismiss the observed relationship between the acidoid content and the base status as accidental it becomes obvious that we are here confronted with a mechanism by which plants are endowed with the power to adjust and adapt themselves in relation to their environment the consequences of which, to the life and growth of plants, are readily perceived, and which places before us a multitude of questions to be answered.

To appreciate the significance of what here has been observed it is necessary that we understand something about the functions of the acidoids.

Though the subject is a complex one and is intended for a special treatment later we shall at the present time add a few words about the functions of the acidoids. It is quite obvious that these functions

are not merely confined to neutralization and fixation of the bases. In the living cell the functions of the acidoids are of vital importance in many ways. The most evident of these are the functions as regulators of the osmotic pressure and of the Donnan potential essential for the electrical transfer of ions.

The cations in combination with, and dissociated by the acidoid constitute the micellar ion atmosphere and it is the concentration of these ions which govern the differences in osmotic pressure and electrical potential between the micellar and the outside solution. The greater the concentration of the micellar ions the greater is, other things being equal, the osmotic pressure and the Donnan potential. But the greater the concentration of free electrolytes the smaller are, other things being equal, the osmotic and potential differences between the inside and outside solutions. Now it can be shown¹ that it requires a higher concentration of free electrolyte to suppress the osmotic and potential differences below a certain value the higher the concentration of the micellar ions, or, putting

¹ From the Donnan equation for univalent ions $x^2 = y(y + z)$ we have at 18° C.

$$\text{P. D.} = 58 \log \frac{x}{y} \text{ millivolts,}$$

Now since the value of $\frac{x}{y}$ depends upon the magnitude of the micellar ion activity z as well as on the activity of the free electrolyte (x = outside, y = inside activity) the effect of the latter on the P. D. can best be illustrated by writing x in terms of y and z thus (Loeb 1924)

$$x = \sqrt{y(y + z)}$$

and

$$\frac{x}{y} = \frac{\sqrt{y(y + z)}}{y} = \sqrt{\frac{y + z}{y}} = \sqrt{1 + \frac{z}{y}}$$

which gives

$$\text{P. D.} = \frac{58}{2} \log \left(1 + \frac{z}{y}\right) \text{ millivolts,}$$

which shows that the greater the activity z of the micellar ions the greater must be the activity of the free electrolyte y in order to suppress the potential by a certain amount.

For the osmotic difference the Donnan equation gives

$$2y + z = 2x.$$

Now

$$2y + z = \sqrt{4y^2 + 4yz + z^2}$$

and

$$x = \sqrt{y^2 + yz} \text{ or } 2x = \sqrt{4y^2 + 4yz}$$

when the difference becomes

$$\sqrt{4y^2 + 4yz + z^2} - \sqrt{4y^2 + 4yz}$$

from which it can be seen that y must be larger the larger the value of z in order to suppress the osmotic difference by a certain amount.

it the other way, it requires a higher micellar ion concentration, i.e., a greater acidoid content, to resist the suppression the greater the concentration of free electrolytes.

From this relationship it follows that the algae growing in sea water need a higher acidoid content than the lichens which grow on the top of a leached soil or on the almost bare rock.

It should be pointed out that the difference in the micellar ion concentration between the algae and the lichens is in reality much greater than indicated by their acidoid contents (= capacity at pH 7). The pH of the algae was 6.62 whereas the lichens had a pH of only 4.89. At this pH the capacity of the lichens to bind NaOH is only about 9 milliequivalents per 100 grams. The capacity of the algae to bind cations in sea water at pH 6.62 is undoubtedly greater than its capacity to bind NaOH at pH 7.

Another fundamental function of the acidoids is in their relation to the cation intake. At the moment the acidoid is synthesized it may be assumed to be unsaturated, i.e., in the form of the free acidoid. The H ions tend to diffuse away much faster than the slow diffusing metal cations can replace them. This gives rise to a very high P.D. A continuous production of acidoids causes a continuous outward flow of H ions and a continuous inward flow of metal cations. TEORELL (1937) has shown in a series of ingenious experiments that by means of a continuous addition of acid to a solution on the inside of a membrane a continuous stream of cation can be made to move against a steep osmotic gradient from a dilute outside salt solution until the inside solution reaches a concentration many times as great.

Nature continuously «adds» acidoids inside the plant membranes especially at the growing point. The acidoid anions cannot diffuse out together with the H ions but cause instead the cations in the outside solution, no matter how dilute, to accumulate inside the plant.

The observations by HOAGLAND (1940) and STEWARD (1937) and their coworkers and by LUNDEGÅRDH (1940) have shown the salt accumulation in plants to be intimately related to the metabolic activities and especially to the growth of the cell or potentiality for cell growth. The salt accumulation is conditioned by active aeration and an abundant supply of carbohydrates. Anaerobic conditions and depletion of carbohydrates lead to little or no accumulation. In mature plants there is only a slight capacity for further accumulation of salt. Since now the same conditions seem to govern the formation of plant acidoids (and, as will be shown later, plant basoids) there is good reason to link the salt accumulation with the formation of protoplasmic acidoids and basoids (ampholytoids).

Hoagland and Broyer could find no evidence of a H ion gradient between the cell sap and the external mediums and therefore dis-

count such an explanation. They admit, however, the formation of organic acids as a metabolic response to a basic residue resulting from an excess of cation accumulation. As far as the acidoid production is concerned a H ion gradient would be expected to be established between the cytoplasm and the vacuole as well as between the cytoplasm and the external medium. Such a gradient between an amphoteric colloid and the surrounding medium does not reveal itself by an ordinary pH determination. The best evidence of the existence of a H ion gradient is found in the exchange acidity obtained at pH above the isoelectric point. In a system where amphoteric colloids are formed there must not only be a H ion gradient but also a OH ion gradient in the same direction but, of course, from different points, i. e., from the basoid groups.

The problem here dealt with raises many practical questions which must be answered. We shall note only a few of them:

What factors other than those here studied affect the acidoid content?

What is the relationship between the acidoid content and the following:

1. Feeding power — should be greater the greater the acidoid formation.
2. Nutrient demands — must be greater the greater the acidoid content.
3. Acidity tolerance — might increase with decrease in acidoids.
4. Salinity tolerance — should go with a high acidoid content.
5. Amount and forms of nitrogen. — The nondialysable N seems to increase with the acidoid content. In eight samples we found the following:

| Litter | Wheat straw | Pine | Beech | Birch | Oak | Maple | Ash | Elm |
|----------------------|----------------|------|-------|-------|------|-------|------|------|
| Acidoids m.e./100 g. | 15 | 38 | 68 | 87 | 89 | 97 | 131 | 147 |
| Nitrogen % | 0.25 | 0.58 | 0.98 | 1.26 | 1.28 | 1.01 | 2.14 | 2.23 |

6. Organic basoids — probably related to nondialysable N.
7. Decomposition — found to increase with acidoid content.
8. Digestibility — probably much the same as the decomposition. The acidoid content of six kinds of mature straw suggests a relationship: Wheat 15, rye 16, oat 22, barley 23, clover 54 and pea 57 m.e. per 100 grams.
9. Structure — The tensile strength appears to be inversely proportional to the acidoid content: consider materials named under points 5 and 8. Sour humus, low in acidoids, is fibrous; mild humus, high in acidoids, is granular. Conclusion: The polar acidoid groups

are formed by breaks in the carbon chain. The greater the polarity the smaller the molecular aggregates:

Humic > Hymatomelanic > Fulvic.

We have found the most characteristic and, therefore, one of the earliest recognized properties of humus, its acidic property, to be of the same nature and to be controlled by the same factors as the acidic properties of plant materials. The dark color of humus has probably been responsible for placing it in an apparently too isolated position. The brown, fibrous »sour» humus is changed into a black, granular »mild» humus by alkaline auto-oxidation, a reaction which, as we have seen, greatly increases the acidoid content.

If, in general, the same relationship between acidoids and non-dialysable nitrogen holds for humus as it does for plant materials, and we have every reason to believe that it does, then we have an explanation to Hilgard's observation that arid humus is richer in nitrogen than humid humus. Aridity means no leaching and no leaching means a high base status. The following relationship may therefore be anticipated:

High base status = high acidoid content = high nitrogen content = low C/N ratio, and, vice versa:

Low base status = low acidoid content = low nitrogen content = high C/N ratio.

Summary.

A study of the factors governing the formation of acidoids in plants and humus has shown the following.

1. Raw humus increases its acidoid content by aerobic decomposition in the presence of calcium carbonate.
2. Treatment of the humus under sterile conditions by alkali increases its acidoid content.
3. Electrodialysed elm and birch leaves reduce their acidoid content in aerobic decomposition.
4. »Sour» humus has a low and »mild» humus a high acidoid content.
5. Acid vegetation such as the podzol flora has a lower acidoid content than plants of higher base status.
6. The highest acidoid content has been found in seaweeds growing in a medium which represents the highest base status.

The functions of the acidoids have been discussed and an attempt is made to explain the relationships observed.

The mechanism of acidoid formation provides the plant with an automatic control of its acid-base balance and with a power to adjust itself to its external environment.

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